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CHEMICAL REACTIONS OF MERCURY IN COMBUSTION FLUE GASES

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ABSTRACT. Atmospheric Hg is present in different physical and chemical forms, which determine its atmospheric transformation and transport capacities. The chemistry of Hg in flue gases is thus of importance for the deposition pattern around point source emissions. In order to apply Hg cleaning methods in flue gases its speciation is also of importance. To investigate this under realistic conditions, a 17 kW propane fired flue gas generator was used, while the kinetics of specific Hg reactions were investigated in a continuous flow reactor. Elemental Hg is readily oxidized by Cl_2 and HCl both at room and at elevated temperatures (up to 900°C) but not by NH_3 , N_2O , SO_2 or H_2S . It reacts with O_2 if a catalyst, such as activated carbon, is present. A slow reaction between Hg and NO_2 has also been noted.

1. Introduction

The total amount of Hg emitted to the atmosphere is difficult to estimate. Problems encountered are related to measurement uncertainties at point sources and to difficulties in estimating diffuse anthropogenic and natural emissions.

The anthropogenic emissions of Hg contain many different forms, depending on the nature of the industrial or combustion process under consideration. In addition there are many other activities in modern society that are giving rise to diffuse emissions of Hg, for example waste deposits, laboratories and dentists.

Elemental Hg and different forms of gaseous and particulate divalent Hg are emitted to the atmosphere. If combustion plants are equipped with flue gas cleaning systems, much of the divalent and particulate Hg is retained. Most countries have not yet built up effective cleaning systems for Hg, however, and as a general approximation one may conclude that about 50% of the anthropogenic Hg emitted is elemental, while 50% is emitted in various divalent forms [1 to 4]. The elemental Hg will add to the atmospheric background concentration, while the divalent gaseous and particulate Hg will have a high tendency to deposit within the region where it is emitted [5, 6].

Dominating point sources for Hg emissions are chlorine alkali factories, waste incineration plants, crematories, coal and peat combustion facilities and smelters. Much of the Hg present in waste originates from batteries, Hg lamps and electronic devices. Untreated waste in an industrialized area may contain $5\text{ }\mu\text{g g}^{-1}$ Hg, while if it is sorted and batteries are extracted, household waste may contain as little as $1\text{ }\mu\text{g g}^{-1}$ Hg [7]. The Hg content in coal and peat usually varies from 0.02 to $1\text{ }\mu\text{g g}^{-1}$ Hg, but can be as high as $3\text{ }\mu\text{g g}^{-1}$ [8].

Most flue gas cleaning systems remove the oxidized Hg forms, including Hg(II) bound to particles, while it is mainly elemental Hg that is emitted. In highly effective cleaning systems, elemental Hg is also oxidized and subsequently removed before the flue gas is emitted to the atmosphere. In combustion processes without flue gas cleaning systems, it is reasonable to assume that 20 to 80 % of the Hg emission is divalent Hg.

All combustion processes generate a mixture of gases and particles. Basically, gases like N_2 , O_2 , H_2O , CO_2 , CO and NO_x are always present in the flue gas. The concentration of NO_x and CO can vary depending on combustion temperature and furnace construction. The presence of other gases such as SO_2 , HCl , Cl_2 , H_2S and NH_3 is more dependent on what the type of fuel being combusted. Table I shows some typical values for gases in coal combustion and waste incineration. The reactions and kinetics of these gases with Hg^0 and $Hg(II)$ at flue gas temperatures have not yet been investigated.

TABLE I. Some typical raw flue gas concentrations in coal combustion and household waste incineration.

	Coal combustion	Waste incineration
O_2	4-10 %	6-15 %
CO_2	10-16 %	5-14 %
CO^*	10-100 $\mu L L^{-1}$	10-100 $\mu L L^{-1}$
NO	100-1000 $\mu L L^{-1}$	100-1000 $\mu L L^{-1}$
NO_2	5-50 $\mu L L^{-1}$	5-50 $\mu L L^{-1}$
SO_2	100-2000 $\mu L L^{-1}$	100-300 $\mu L L^{-1}$
HCl	1-100 $\mu L L^{-1}$	400-1000 $\mu L L^{-1}$
NH_3	5 $\mu L L^{-1}$	<1 $\mu L L^{-1}$
N_2O	5-200 $\mu L L^{-1}$	<1 $\mu L L^{-1}$
Hg	1-5 $\mu g m^{-3}$	100-1000 $\mu g m^{-3}$

* The CO concentration may be much higher during short time intervals.

The speciation of Hg in flue gases is dependent on temperature, residence time and the presence of other flue gas components such as HCl and SO_2 . Sampling of Hg is usually performed using absorption solutions that retain oxidized Hg forms directly and elemental Hg after oxidation. Separation of different Hg species by means of different absorption solutions is difficult, especially in flue gases from coal combustion, since the Hg concentration is low and the flue gas contains large amounts of SO_2 that can disturb the analysis. A number of methods have been suggested through the years. Two standard approaches are the permanganate and persulphate methods [2]. The disadvantage of all batch methods is that no time resolution better than $\sim 1/2$ hour mean values can be obtained. Two continuous methods are available: Continuous Cold Vapour Atomic Absorption (CVAA) spectroscopy [1, 2] and Differential Optical Absorption Spectroscopy (DOAS) [2], the latter being only applicable for elemental Hg .

The objective of this study has been to investigate the transformation of mercury in flue gases and to get a further understanding of the basic reactions involved. This is important from the environmental point of view and for the development of methods for Hg abatement.

2. Experimental

Two different experimental set-ups have been used to investigate Hg reactions, namely a 17 kW flue gas generator and a continuous flow reactor system for more detailed investigation of the basic reactions.

2.1. SIMULATED FLUE GASES

The 17 kW flue gas generator [cf. also 1] consists of a propane-fired burner and a 12 m long flue gas duct provided with a number of probes along the pipe for recording O_2 concentration and for gas sampling. The temperature, decreasing along the duct, is measured with thermocouples. Trace gases such as vaporized Hg , HCl , SO_2 etc, can be admitted to the flue gas generator near the

burner. A system of flow meters is used to adjust the concentration of these gases. The total gas flux is about 750 L min^{-1} (NTP).

The continuous CVAA spectroscopic method has been used for analysis of both Hg^0 and total Hg in the flue gas [1]. To analyze the elemental Hg, a flow of 1 L min^{-1} is drawn via a PTFE tube to a refrigerated (by ice) gas/liquid separator, where condensed water is separated from the flue gas. Since Hg^0 has low solubility in water all the Hg-vapour is transferred into the 120 cm long analysis cell. The light from a low pressure Hg lamp is absorbed by the Hg^0 -vapour at 253.7 nm. The light passes a filter with a bandwidth of 10 nm to a photomultiplier. The detection limit is $3 \mu\text{g Hg m}^{-3}$.

The total amount of Hg is measured via another line where the flue gas sample is brought in contact with an acidic 0.5 M SnCl_2 -solution. Oxidized compounds of Hg are here reduced to elemental Hg. The Sn(II) -chloride solution is separated together with the condensed water in a second gas/liquid separator and the Hg vapour proceeds to the analysis cell. The Sn(II) -solution will not reduce certain stable compounds such as HgS , which will not be included in the following results.

2.2 THE CONTINUOUS FLOW REACTOR SYSTEM

The flow reactor system consists of a pre-warming section and a 45 cm long quartz reactor, placed in two furnaces (Figure 1). The temperature is measured using two thermocouples (Chrom Nickel-Chrom) and controlled by two microprocessors (type Eurotherm 818) which keep the temperature within 0.5°C of a preset value. A system of flow meters is used to regulate the gas concentrations. Reactant gases are premixed in two separate lines using N_2 as matrix gas. The flow rate through the reaction cell is about 1 L min^{-1} .

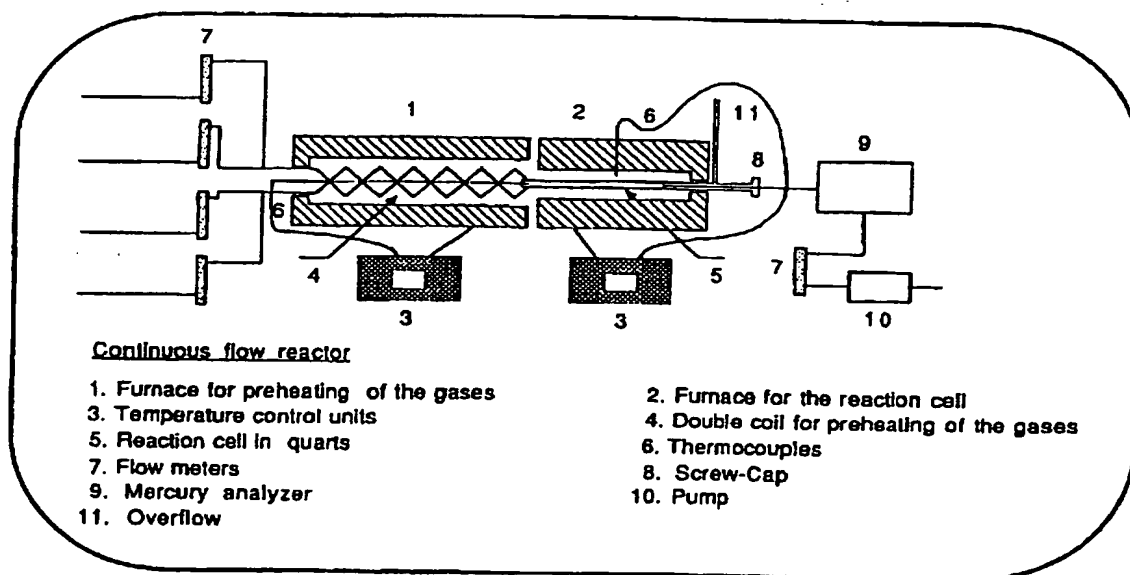


Figure 1. Schematic drawing of the experimental set-up.

The concentration of elemental Hg was measured with the CVAA technique and the decrease of elemental Hg due to the reactions between Hg and the different trace gases was continuously recorded during the experiments. The initial concentration of Hg was obtained by passing N_2

through a thermostated coil containing several droplets of Hg. The vapour pressure of the Hg, the flow rate of N₂ through the coil and the dilution flow rate then determines the final Hg concentration.

3. Hg reactions with flue gas components

In order to study the reactivity of Hg with flue gas components, experiments were performed in the flue gas generator with O₂, HCl, Cl₂, SO₂ and NO₂. Subsequently, isolated reactions with O₂, HCl, Cl₂, NO, NO₂, NH₃, SO₂ and H₂S were investigated under more controlled conditions in the continuous flow reactor. In all experiments the gas concentrations were maintained in a typical range for combustion processes e.g. coal combustion or waste incineration. The reactions will be discussed in this chapter, but the main results are summarized in Figure 2.

Mercury Reactions	
$2 \text{ Hg(g)} + \text{O}_2\text{(g)} \Rightarrow 2 \text{ HgO(s,g)}$	(10%)
$\text{Hg(g)} + \text{Cl}_2\text{(g)} \Rightarrow \text{HgCl}_2\text{(s,g)}$	(10 $\mu\text{L L}^{-1}$)
$2 \text{ Hg(g)} + \text{Cl}_2\text{(g)} \Rightarrow \text{Hg}_2\text{Cl}_2\text{(s)}$	(10 $\mu\text{L L}^{-1}$)
$\text{Hg(g)} + 2 \text{ HCl(g)} \Rightarrow \text{HgCl}_2\text{(s,g)} + \text{H}_2\text{(g)}$	(300 $\mu\text{L L}^{-1}$)
$2 \text{ Hg(g)} + 4 \text{ HCl(g)} + \text{O}_2\text{(g)} \Rightarrow 2 \text{ HgCl}_2\text{(s,g)} + 2 \text{ H}_2\text{O(g)}$	(300 $\mu\text{L L}^{-1}$)
$4 \text{ Hg(g)} + 4 \text{ HCl(g)} + \text{O}_2\text{(g)} \Rightarrow 2 \text{ Hg}_2\text{Cl}_2\text{(s)} + 2 \text{ H}_2\text{O(g)}$	(300 $\mu\text{L L}^{-1}$)
$\text{Hg(g)} + \text{NO}_2\text{(g)} \Rightarrow \text{HgO(s,g)} + \text{NO(g)}$	(300 $\mu\text{L L}^{-1}$)
$\text{Hg(g)} + \text{NH}_3\text{(g)} \Rightarrow \text{No reaction}$	(500 $\mu\text{L L}^{-1}$)
$\text{Hg(g)} + \text{N}_2\text{O(g)} \Rightarrow \text{No reaction}$	(300 $\mu\text{L L}^{-1}$)
$\text{Hg(g)} + \text{SO}_2\text{(g)} \Rightarrow \text{No reaction}$	(115 $\mu\text{L L}^{-1}$)
$\text{Hg(g)} + \text{H}_2\text{S(g)} \Rightarrow \text{No reaction}$	(300 $\mu\text{L L}^{-1}$)

Figure 2. Proposed reactions between elemental Hg and some gases. The maximum experimental concentrations of the reactant gases are given in brackets. The temperature range was 20 to 900 °C and the inlet Hg concentration was 100 $\mu\text{g m}^{-3}$ (NTP).

3.1. Hg REACTIONS WITH HCl(g)

The reaction between Hg and gaseous HCl is of special interest in waste incineration and in combustion of coal of marine origin since high levels of HCl(g) are present in both cases. The influence of the HCl(g) concentration on the reaction rate has been studied both in the flue gas generator and in the continuous flow reactor with similar results (Figures 3 and 4).

In the flue gas generator, the Hg concentration was measured at a sampling point where the temperature was approximately 500°C . The HCl -concentration was varied up to $150\ \mu\text{L L}^{-1}$ and the O_2 -concentration was 10%. Since the residence time for the gas at this point is around 1.5 s, the result in Figure 3 indicates a relatively fast reaction occurring at a rather high reaction temperature. The concentration of total Hg is nearly constant, which proves that a gaseous compound is formed, probably $\text{HgCl}_2(\text{g})$.

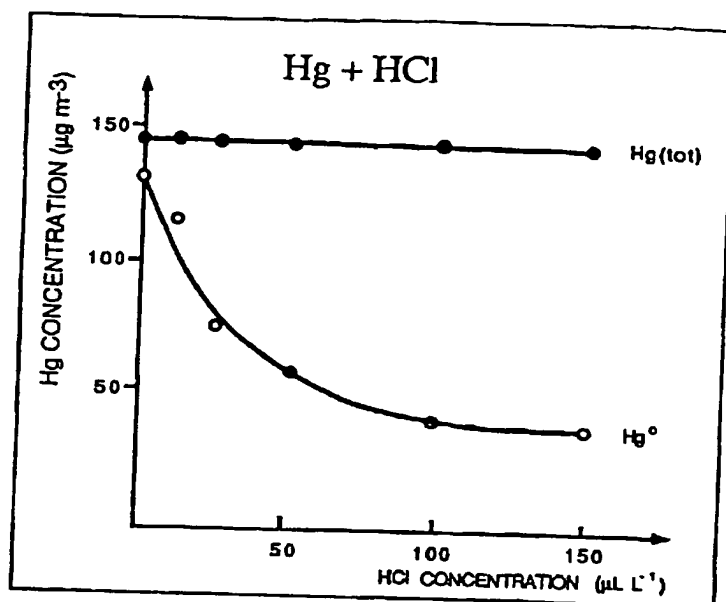


Figure 3. Concentration of Hg vs. concentration of HCl(g) in the flue gas generator at a temperature of 500°C

In the continuous flow reactor, similar experiments have been performed at constant temperatures which are not possible to obtain in the flue gas generator, since a temperature gradient exists from the burner through the duct. The results are summarized in Figure 4. The reaction rate increases with increasing temperature, and at 900°C more than 90 % of the gaseous Hg is oxidized in less than 1 s.

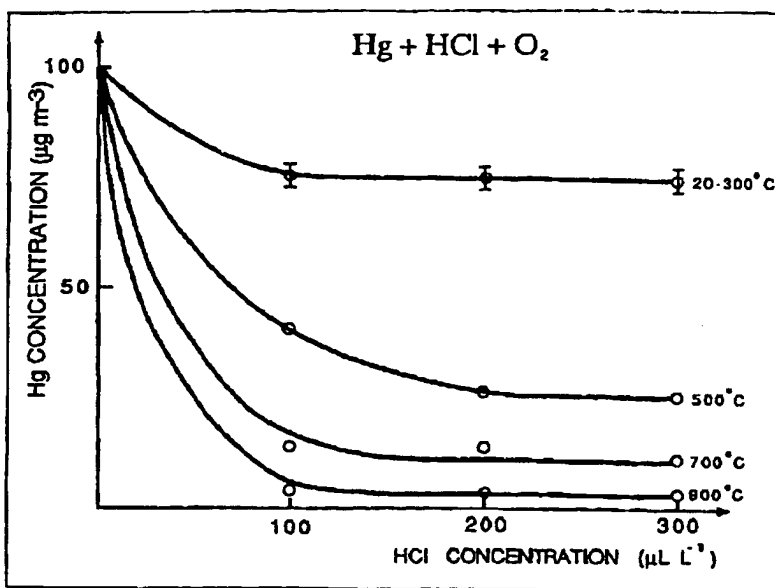
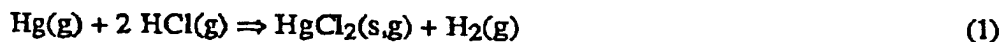
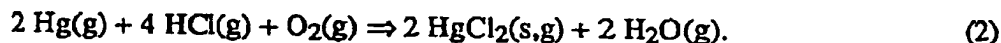


Figure 4. Concentration of elemental Hg vs. concentration of HCl(g) in the presence of 10 % O₂(g) at different temperatures. The reaction time is ranging from 0.7 s at 900 °C to 2.8 s at 20 °C.

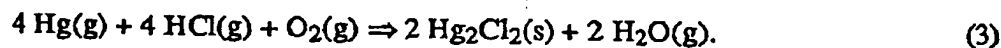
The reaction path for this system is not evident. A direct trimolecular reaction (1),



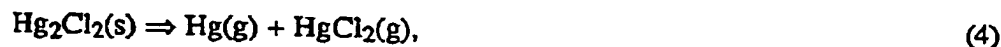
or a sum of simpler elementary reactions may occur, but this reaction is not thermodynamically favourable at temperatures above 300 °C. Trimolecular reactions are not common in general, and usually quite slow, which makes them rather unlikely in combustion processes where the reaction time is short. A more favourable reaction involving O₂ is given by reaction (2).



This reaction is thermodynamically forced to the right at temperatures up to at least 800 °C. It is obvious that (2) is an overall reaction, involving a number of elementary reactions. Another possible overall reaction is the formation of calomel, Hg(I)chloride, instead of Hg(II)chloride.



Since calomel decomposes at around 400 °C (cf. Table II) through reaction (4)



it may only exist below this temperature.

3.2. Hg REACTIONS WITH $\text{Cl}_2(\text{g})$

Mercury reacts readily with Cl_2 [9-11]. Figure 5 shows typical results from the flue gas generator with different Cl_2 concentrations. The experiment is done at a temperature around 500°C . The reaction time at this point is around 1.5 s. About 70% of the initial elemental Hg concentration is oxidized at this point while the total Hg concentration is constant, which indicates that a gaseous product is formed. Figure 6 shows the results from a similar experiment in the continuous flow reactor but at different constant temperatures.

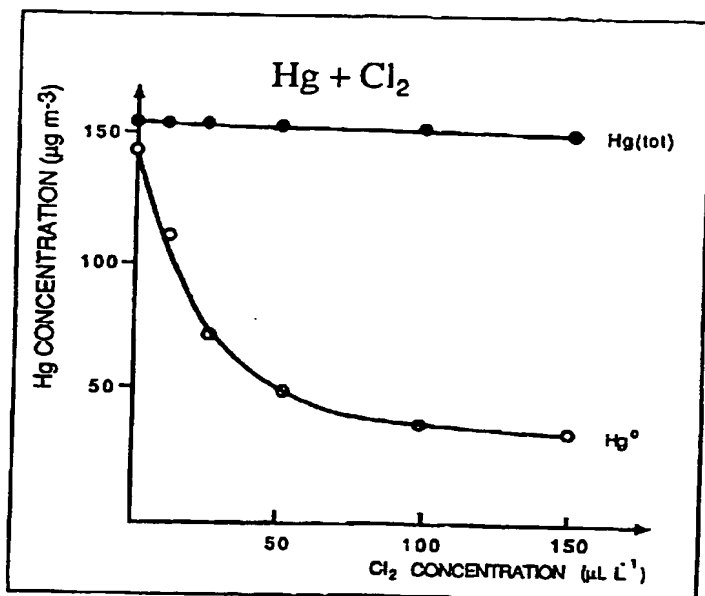


Figure 5. Hg concentration vs. Cl_2 concentration in the flue gas generator at 500°C .

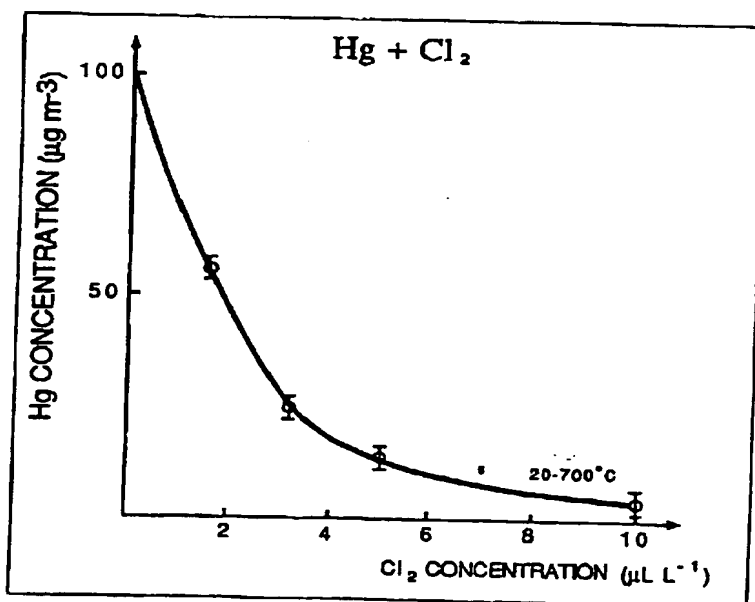


Figure 6. Hg concentration vs. Cl_2 concentration at different temperatures. The reaction time ranges from 0.8 s at 700°C to 2.8 s at 20°C .

These experiments show that Hg reacts with Cl_2 even at 20 °C. This makes the evaluation of the experimental data from the continuous flow reactor difficult, since the reaction also proceeds in the CVAA cell operating at room temperature.

The results from the flue gas generator may also be misleading, since the oxidation may continue in the analysis cell or in the teflon tubing. The constant value of the total Hg contradicts this, however. If oxidation occurs in the analysis cell, it should lead to a decrease also in the total Hg signal, since only elemental Hg contributes to the absorption at 253.7 nm. The explanation is probably that Cl_2 is dissolved in the aqueous condensate and removed in the gas/liquid separator [1]

As for the previous system Hg(I) and (II) chlorides are the most probable products from the reaction with Cl_2 .



The experimental results indicate that heterogeneous reactions are important, especially at low temperatures. This is judged from the observation that several trials must be performed to obtain reproducible results. This is probably due to the formation of a product on the surface of the reaction cell, which influences the rate of the overall reaction. This is also in agreement with results obtained by Medhekar *et.al.* [11].

3.3. Hg REACTIONS WITH $\text{NO}_2\text{(g)}$

NO_x is formed in all combustion processes. At high temperatures NO is the dominant species [12] but NO_2 may also be present to some extent ($\sim 10 \mu\text{L L}^{-1}$).

The experiments were performed with a NO_2 -concentration of 350 to 1000 $\mu\text{L L}^{-1}$. The NO_2 was fed into the combustion chamber, and since it is not thermally stable at this temperature (800 to 1000 °C), it will start to decompose. The given NO_2 -concentration should therefore only be regarded as a NO_x concentration. $\text{NO}_2\text{(g)}$ starts to decompose at 150 °C (cf. reaction (7)) and at 600 °C the decomposition should be complete.



However, this reaction is not sufficiently fast for equilibrium to be reached on the time-scale available in the flue gas generator [13]. An estimate is that 50 to 75 % of the NO_2 probably is decomposed at the sampling point at 340 °C.

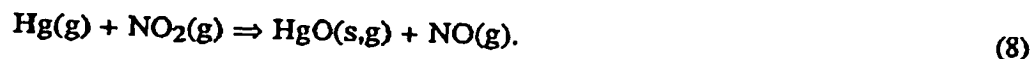
A small but significant oxidation occurs in the flue gas generator when $\text{NO}_2\text{(g)}$ is added (cf. Figure 7). At temperatures above 500 °C there is no further oxidation of the Hg, but at 340 °C with an initial NO_2 concentration of 1000 $\mu\text{L L}^{-1}$, 11% of the mercury is oxidized. This indicates a much lower reaction rate than in the case of $\text{Cl}_2\text{(g)}$ and HCl(g) . There are several possible reaction products in the Hg + NO_2 system, including Hg nitrites and nitrates [14] but most of them are unstable over 200 °C (cf. Table II).

TABLE II. Thermochemical behaviour for some Hg compounds.

Compound	Melting point °C	Boiling point °C	Decomposition °C	Ref.
Hg ⁰	-38.87	356.58	-	15
HgO	-	-	500 ¹	15, 16
HgCl ₂	276	302	1227=15% ²	15, 17
Hg ₂ Cl ₂	-	-	subl. 400	15
HgS	-	-	subl. 583.5	15
Hg ₂ O	-	-	100	15
Hg ₂ (NO ₂) ₂	-	-	100	15
Hg(NO ₂) ₂	-	-	100	18
Hg ₂ (NO ₃) ₂ *2H ₂ O	70	-	-	15
Hg(NO ₃) ₂	-	-	160	19

1. $\log P(\text{tot}) = -5273.5/T + 1.75 \cdot \log T - 0.001033 \cdot T + 5.9461$ (P in Torr).
 2. $\log K_p = 5.141 - 10176/T$.

A probable reaction is the formation of HgO(s,g):



This is in agreement with the observed experimental behaviour, since no reaction occurred at temperatures above 500 °C, where HgO is thermodynamically unstable.

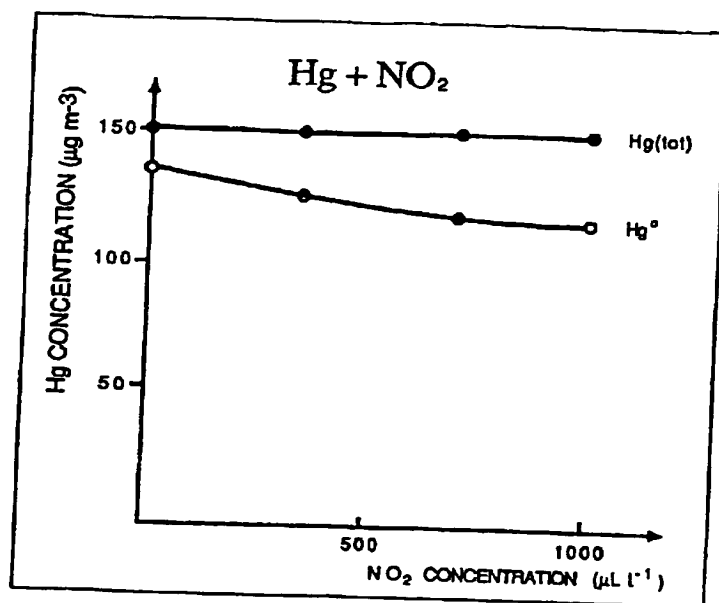


Figure 7. Concentration of Hg vs. concentration of NO₂ at a temperature of 340 °C in the flue gas generator. The NO₂ concentration should be regarded as a NO_x concentration.

3.4. Hg REACTIONS WITH O₂(g)

It has previously been reported [1] that a significant oxidation occurs in the flue gas generator even when no reactive trace gases were added to the flue gas. This effect was strongly enhanced when activated carbon was added. When similar experiments were performed in a "clean" reaction cell in the continuous flow reactor, no reaction was detected. The temperature range was 20 to 700 °C and the O₂ concentration was varied up to 10 %.

No reaction was found either, when 1 g of α -Al₂O₃ wool was placed in the reactor. However, when 1 g activated carbon (spec. surface= 900 m² g⁻¹, size 0.9 to 1.1 mm) was added into two quartz vessels with dimensions 5 x 50 mm and placed in the reaction cell, an oxidation of the Hg⁰ was observed.

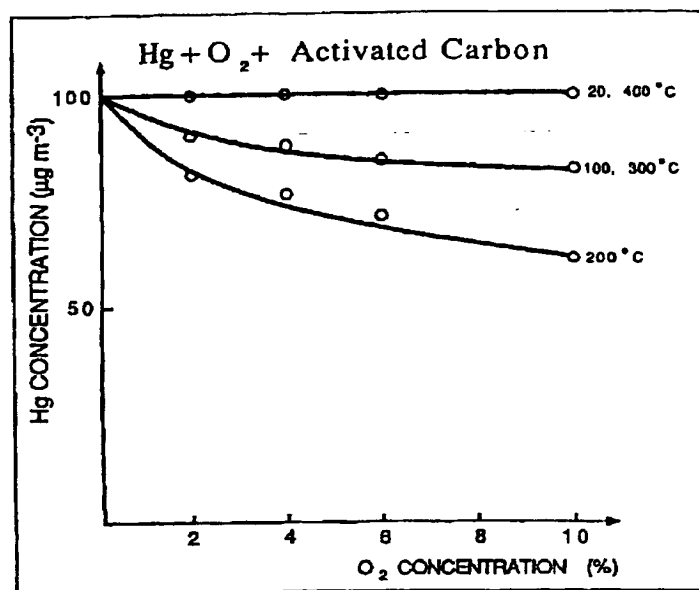


Figure 8. Concentration of Hg vs. concentration of O₂ with 1 g of activated carbon present. Reaction time < 5 s.

As seen in Figure 8, the reaction proceeds at a measurable rate in the temperature range 100 to 300 °C. At 20 °C the reaction rate is probably too slow, while at 400 °C the formation of HgO is not believed to be favourable. Around 200 °C, the reaction rate is at maximum, which indicates that different processes determine the rate of this reaction at different temperatures:

- Adsorption of Hg(g) on the surface (decreases with increased temperature).
- Reaction between Hg(ads) and O₂(g) (increased reaction rate with increased temperature up to the decomposition temperature).

This could also be written



The most likely reaction product in this system is HgO(s,g).

3.5. Hg REACTION WITH SO₂, H₂S, N₂O AND NH₃

No reaction could be detected between Hg and SO₂, H₂S, N₂O and NH₃. This is not unexpected due to their reducing or inert character.

The experimental conditions are summarized in Table III

TABLE III. Experimental condition for the reaction of mercury with SO₂, H₂S, N₂O and NH₃.

Trace gas	Max. Conc.($\mu\text{L L}^{-1}$)	Temp. Range ($^{\circ}\text{C}$)	Reaction time(s)
SO ₂	115	20-900	4.8-1.2
H ₂ S	270	20-900	2.2-0.5
N ₂ O	300	20-800	4.8-1.3
NH ₃	500	20-600	2.6-0.9

4. Conclusions

Hg reacts with Cl₂, HCl, NO₂ and O₂ but not with NH₃, N₂O, SO₂ or H₂S (Figure 2). In practice, this means that Hg could be oxidized by a number of different routes in a real combustion facility.

The results indicate that, in waste incineration, with high concentrations of chloro compounds (c.g. HCl, Cl₂), the main part of the Hg content will be oxidized by these species. In coal combustion, with low concentrations of HCl and Cl₂, a slight oxidation could occur by NO₂. In filters containing soot and other particles with a large surface area, O₂ will cause a considerable oxidation if the filter acts at about 200 $^{\circ}\text{C}$, which is common in many combustion plants.

These findings are of importance for the design of flue gas cleaning systems for waste incineration, and to estimate which Hg species are emitted from a specific combustion plant.

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